Bimetallic Systems. Part 7.[1] Platinum and Palladium Dicyanides containing Terminal or Bridging $Ph_2PCH_2PPh_2$ and Heterobimetallics with Silver, Gold, Mercury, Rhodium, Iridium, or Molybdenum

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Treatment of $[M(Ph_2PCH_2PPh_2\text{-}PP')_2]Cl_2$, *i.e.* $[M(dppm\text{-}PP')_2]Cl_2$, with NaCN gives $[M(CN)_2(dppm\text{-}P)_2]$ (M = Pt or Pd). These complexes are fluxional at 20 °C due to rapid 'end over end' motion of the dppm ligands. The complex $[MCl_2(dppm\text{-}PP')]$ with NaCN gives the binuclear 'face to face' complexes $[M_2(CN)_4(\mu\text{-dppm})_2]$. The platinum complex $[Pt(CN)_2(dppm\text{-}P)_2]$ is quaternized by methyl iodide to give $[Pt(CN)_2(Ph_2PCH_2PMePh_2)_2]I_2$. With $AgNO_3$, followed by NaI, $[Pt(CN)_2(dppm\text{-}P)_2]$ gives $[(NC)_2Pt(\mu\text{-dppm})_2AgI]$, with $[AuCl(PPh_3)]$ it gives $[(NC)_2Pt(\mu\text{-dppm})_2Au]Cl$, and with $HgCl_2$ it gives $[(NC)_2Pt(\mu\text{-dppm})_2HgCl_2]$. The complexes $[M(CN)_2(dppm\text{-}P)_2]$ (M = Pt or Pd), when treated with $[Rh_2Cl_2(CO)_4]$, $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}p)]$, or *trans*-$[IrCl(CO)(PPh_3)_2]$, give heterobimetallics of type $[(NC)_2M(\mu\text{-dppm})_2M'(CO)Cl]$ (M′ = Rh or Ir). Treatment of $[Pd(CN)_2(dppm\text{-}P)_2]$ with $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cyclohepta-1,3,5-triene) gives $[(NC)_2Pd(\mu\text{-dppm})_2Mo(CO)_3]$. I.r. and ^{31}P and ^1H n.m.r. data are given.

We have used bis(diphenylphosphino)methane (dppm) as a bridging ligand for the systematic synthesis of hetero- and homo-bimetallic complexes: one method we have developed has been to co-ordinate two dppm ligands in a monohapto fashion to one metal and to use the two free phosphorus atoms to complex to a second metal. For platinum and palladium, neutral or charged complexes of type $[MX_2(dppm\text{-}P)_2]^{n+}$ (M = Pt or Pd; n = 0, X = C≡CR or R; n = 2, X =CNR; R = alkyl or aryl) are suitable.[2–8] Necessary properties of the associated ligands X are that they must be strongly bonded to M and not easily displaced as X^-, and that they must prevent chelation of dppm to M with formation of a four-membered chelate ring. Cyanide ion seemed a suitable candidate for such a ligand since it has a high affinity for platinum(II) or palladium(II) and seems to have a strong preference for *trans* co-ordination in complexes of type *trans*-$[M(CN)_2(PR_3)_2]$ (M = Pt or Pd), properties which should stabilize monohapto dppm complexes relative to chelates. In the present paper we report on the formation of such monohapto complexes and on related mononuclear species, and on the formation of homo- and hetero-bimetallic complexes of platinum or palladium dicyanides. A preliminary account of some of this work has been published.[4]

Results and Discussion

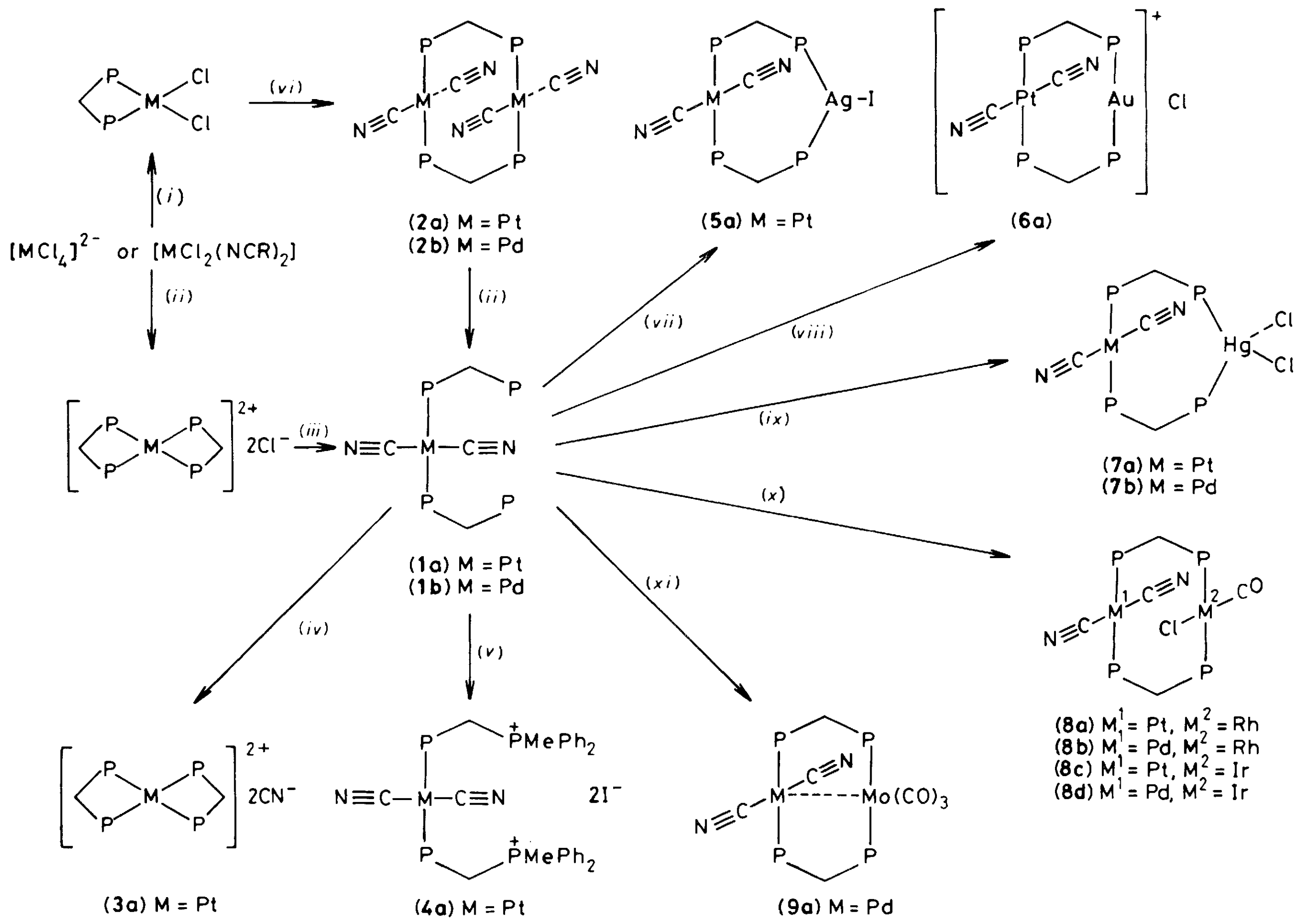
For convenience the various syntheses and transformations are summarized in the Scheme. Known salts of the type $[M(dppm\text{-}PP')_2]Cl_2$ (M = Pt or Pd) are readily prepared from dppm and either $[MCl_4]^{2-}$ or $[MCl_2(NCR)_2]$ (R = Bu^t, M = Pt; R = Ph, M = Pd).[6] We find that treatment of a methanol solution of $[Pt(dppm\text{-}PP')_2]Cl_2$ with 2 equivalents of sodium cyanide gives a crystalline precipitate of the required monohapto complex, *trans*-$[Pt(CN)_2(dppm\text{-}P)_2]$ (**1a**), in excellent (94%) yield and purity (see Experimental section for details and Table 1 for analytical data). The complex showed an i.r. absorption band at 2 125 cm^{-1} (Nujol mull) due to ν(C≡N). This complex was found to be non-conducting in dichloromethane solution and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy showed it to be fluxional. At 20 °C the platinum complex showed two very broad resonances ($w_{\frac{1}{2}}$ *ca.* 250 Hz) at −23.5 and +7.4 p.p.m. but no satellites due to coupling to platinum-195 could be seen presumably because of insufficient signal/noise and the broadness of the resonances. However, at −25 °C the $^{31}P\text{-}\{^1H\}$ n.m.r. pattern corresponds to static structure (**1a**) and the value of $^1J(PtP)$ is consistent with a *trans* arrangement:[9] the chemical shift of the unco-ordinated P atom is very close to that of free dppm. The resonances are deceptively simple triplets due to virtual coupling in the AA′XX′ spin system. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[Pt(CN)_2(dppm\text{-}P)_2]$ in 1,1,2,2-tetrachloroethane at 100 °C consisted of a single broad resonance at δ = −8.35 p.p.m. ($w_{\frac{1}{2}}$ = 125 Hz) with ^{195}Pt satellites, $^1J(PtP)$ = 1 172 Hz. The observation of coupling to ^{195}Pt near to the fast-exchange limit shows that the process is intramolecular and corresponds to rapid 'end over end' exchange, *viz.* $PtPh_2\overset{*}{P}CH_2PPh_2 \rightleftarrows PtPh_2PCH_2\overset{*}{P}Ph_2$. During the course of the measurement of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra in $C_2H_2Cl_4$ at 100 °C substantial decomposition to the binuclear 'face to face' complex $[Pt_2(CN)_4(\mu\text{-dppm})_2]$ (**2a**) and other, uncharacterized, products occurred.

We find that the colourless neutral complex (**1a**) dissolves in nitromethane or nitrobenzene to give the yellow isomeric, ionic complex $[Pt(dppm\text{-}PP')_2][CN]_2$ (**3a**). This was characterized in solution by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy and showed a 1:4:1 triplet pattern with virtually the same chemical shift and value of $^1J(PtP)$ as the corresponding dibromide or di-iodide salts $[Pt(dppm\text{-}PP')_2]X_2$ (X = Br or I). The dicyanide salt (**3a**) could be precipitated from a nitromethane solution by addition of diethyl ether but was not obtained pure.

Addition of sodium cyanide to a methanol solution of $[Pd(dppm\text{-}PP')_2]Cl_2$ gave the colourless, crystalline monohapto dppm complex $[Pd(CN)_2(dppm\text{-}P)_2]$ (**1b**). Microanalytical data are in Table 1. This palladium complex showed an i.r. absorption band at 2 122 cm^{-1} and, like the platinum complex, it is fluxional corresponding to rapid 'end over end' exchange of the monohapto dppm ligands, *viz.* $PdPh_2\overset{*}{P}CH_2PPh_2 \rightleftarrows PdPh_2PCH_2\overset{*}{P}Ph_2$. At −80 °C the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum corresponds to the static structure (**1b**), see Figure. We find that the palladium complex (**1b**) does not ionize in nitromethane solution, in contrast to the platinum complex.

The platinum complex *trans*-$[Pt(CN)_2(dppm\text{-}P)_2]$ (**1a**) was readily quaternized by methyl iodide to give the insoluble dimethiodide complex (**4a**). The value of ν(C≡N) at 2 132 cm^{-1} is typical of a C≡N group and shows that the P, and not the N, has been quaternized.

We prepared the binuclear 'face to face' complexes of type $[M_2(CN)_4(\mu\text{-dppm})_2]$ (M = Pt or Pd) as follows. Treatment of



Scheme. (*i*) 1 mol dppm; (*ii*) 2 mol dppm; (*iii*) 2 mol NaCN in methanol at *ca.* 20 °C; (*iv*) dissolve in nitromethane or nitrobenzene; (*v*) MeI; (*vi*) 2 mol NaCN in boiling ethanol (Pt) or methanol (Pd); (*vii*) $AgNO_3$ followed by NaI; (*viii*) $[AuCl(PPh_3)]$ in tetrahydrofuran; (*ix*) $HgCl_2$ in tetrahydrofuran; (*x*) $[Rh_2Cl_2(CO)_4]$ or $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}p)]$ (platinum complex) or *trans*-$[IrCl(CO)(PPh_3)_2]$ (palladium complex); (*xi*) $[Mo(CO)_3(C_7H_8)]$

$[PtCl_2(dppm\text{-}PP')]$ with sodium cyanide in boiling ethanol or 2-methoxyethanol for several hours gave $[Pt_2(CN)_4(\mu\text{-dppm})_2]$ (**2a**). This formulation is based on: (*i*) elemental analysis (C, H, and N; Table 1); (*ii*) a strong single band, at 2 132 cm^{-1} in the i.r. spectrum due to ν(C≡N); (*iii*) the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum which showed a singlet at δ −1.0 p.p.m. and complex satellites characteristic of a binuclear $Pt_2(\mu\text{-dppm})_2$ moiety; (*iv*) the ^1H n.m.r. spectrum which showed a multiplet at δ 4.6 p.p.m., that was simplified by ^{31}P decoupling into a triplet with relative intensities *ca.* 8:18:8; the outer lines of the theoretical *ca.* 1:8:18:8:1 quintet could not be observed because of insufficient signal/noise ratio in the spectrum. The complex was insufficiently soluble for a molecular-weight determination but there can be little doubt that it is binuclear and of structure (**2a**): analogous tetra-acetylides of type $[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ have been well characterized.[6] Similarly, treatment of $[PdCl_2(dppm\text{-}PP')]$ with NaCN in boiling methanol gave $[Pd_2(CN)_4(\mu\text{-dppm})_2]$, assigned structure (**2b**) on the basis of elemental analysis, i.r., and n.m.r. data (Tables); in particular the ^1H n.m.r. spectrum showed a 'virtually coupled' 1:4:6:4:1 quintet with separation of the peaks of 4.5 Hz due to the PCH_2P resonances.

Heterobimetallic Complexes from $[M(CN)_2(dppm\text{-}P)_2]$ (M = Pt *or* Pd).—Treatment of $[Pt(CN)_2(dppm\text{-}P)_2]$ with a solution of silver nitrate gave what was probably a mixed-platinum–silver cationic complex $[(NC)_2Pt(\mu\text{-dppm})_2Ag]^+$, which was not isolated, but treated with sodium iodide to give the neutral complex $[(NC)_2Pt(\mu\text{-dppm})_2AgI]$ (**5a**), isolated in 76% yield: characterizing data are in the Tables.

Similar treatment of *trans*-$[Pt(CN)_2(dppm\text{-}P)_2]$ with $[AuCl(PPh_3)]$ in dichloromethane gave the platinum–gold complex $[(NC)_2Pt(\mu\text{-dppm})_2Au]Cl$ (**6a**) in excellent (>90%) yield. Further details in the Experimental section and Tables.

We similarly made the Pt–Hg (**7a**) and Pd–Hg (**7b**) complexes by treating $[M(CN)_2(dppm\text{-}P)_2]$ with $HgCl_2$ in tetrahydrofuran: details in Experimental section, characterizing n.m.r. and analytical data in Tables. These complexes are analogous to the diacetylide complexes $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2Au]Cl$ or $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (R = alkyl or aryl) which we have described previously.[6] Interestingly, the mercury–palladium dicyanide complex (**7b**) is much more stable thermally than the corresponding mercury–palladium diacetylide complexes, which are unstable at *ca.* 20 °C.[10] We have also found that the bis-dppm salt, $[Pt(dppm\text{-}PP')_2]Cl_2$ undergoes a ring-opening reaction when treated with $Hg(CN)_2$ to give the platinum–mercury complex (**7a**). Mercury acetylides or mercury(II) acetate–acetylene combinations similarly open up $[Pt(dppm\text{-}PP')_2]Cl_2$ to give heterobimetallic mercury–platinum diacetylides.[6,11]

Treatment of $[Pt(CN)_2(dppm\text{-}P)_2]$ with $[Rh_2Cl_2(CO)_4]$ gave a neutral complex, which we formulate as the 'face to face' complex (**8a**). This formulation follows from the elemental analytical data (C, H, N, and Cl), the non-conductivity in nitrobenzene solution, the $^{31}P\text{-}\{^1H\}$ n.m.r. AA′BB′X pattern, with satellites due to further splitting by platinum-195, and the

Table 1. Microanalytical,[a] melting point,[b] and electrical conductivity data[c]

Complex	M.p. (°C)	Analysis/%				Λ/ohm^{-1} cm^2 mol^{-1}
		C	H	N	Halogen	
(*a*) Platinum						
(1a)	n.d.	60.4 (60.7)	4.45(4.6)	2.7 (2.65)		
(2a)	316—319	51.45(51.35)	3.5 (3.5)	4.95(4.45)		
(4a)	n.d.	50.0 (49.95)	4.05(3.9)	2.15(2.15)	19.0(19.5)	
(5a)	288—291	50.05(49.95)	3.65(3.55)	1.95(2.25)		
(6a)	201—205	47.8 (47.05)	3.45(3.5)	2.0 (1.95)		17
(7a)	275—278	47.9 (48.5)	3.7 (3.45)	2.45(2.15)	3.7(3.45)	
(8a)	230—240	53.95(53.85)	3.75(3.75)	2.55(2.35)	3.3(3.0)	0.3
(8c)	n.d.	49.7 (50.1)	3.35(3.5)	2.1 (2.2)	3.2(2.8)	
(*b*) Palladium						
(1b)	n.d.	67.45(67.35)	3.1 (3.0)	4.95(4.8)		
(2b) ·1.5 $CHCl_3$[d]	217—219	52.3 (52.65)	3.6 (3.65)	4.25(4.45)	12.1(12.6)	
(8b)	212—214	57.85(58.2)	4.15(4.05)	2.5 (2.55)		0.9
(8d)	n.d.	53.5 (53.8)	3.65(3.75)	2.05(2.35)	2.7(3.0)	
(9a) ·0.5 CH_2Cl_2[d]	n.d.	57.85(58.0)	3.7 (3.95)	2.7 (2.45)		

[a] Calculated values (%) in parentheses. [b] Corrected, all melted with decomposition. n.d. = Not determined. [c] In nitrobenzene solution at 20 °C. [d] The presence of solvent molecules was shown by ^1H n.m.r. spectroscopy.

Table 2. $^{31}P-\{^1H\}$ n.m.r. data[a]

Complex	Solvent	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_B)$	$^3J(PtP_B)$	N[b]	Other
(*a*) Platinum							
(1a)	$CDCl_3$ (−25 °C)	+7.1	2 329	−26.5	n.r.	73	
(2a)[c]	CD_2Cl_2	−1.0	2 507		−46		
(5a)	CD_2Cl_2	+11.3	2 334	−8.8	n.r.		$^1J(AgP_B)$ *ca.* 400
(6a)	CD_2Cl_2	+26.6	2 380	+6.2	54	52	
(7a)	CD_2Cl_2	+7.0	2 402	+18.3	185	71	$^1J(HgP_B)$ 5 566
(8a)	CD_2Cl_2	+1.4	2 531	+20.9	n.r.	42	$^1J(RhP_B)$ 149
(8c)	CD_2Cl_2	−2.5	2 852	−28.9	125	92	
(*b*) Palladium							
(1b)	CD_2Cl_2 (−80 °C)	+16.9		−26.9		93	
(2b)	CD_2Cl_2	+11.4					
(7b)	CD_2Cl_2	+16.6		+21.1		64	$^1J(HgP_B)$ 5 251
(8b)	CD_2Cl_2	−3.6		+7.2		91	$^1J(RhP_B)$ 95
(8d)	CD_2Cl_2	+6.7		−19.0		93	
(9a)	CD_2Cl_2	+19.6		+38.4		104	

[a] Spectra (40.25 MHz) measured at +21 °C unless stated otherwise: chemical shifts (δ) in p.p.m., ±0.1 to high frequency of 85% H_3PO_4, and coupling constants (*J*) in Hz (±3); n.r. = not resolved. [b] $N = {}^2J(P_AP_B) + {}^4J(P_AP_{B'})$. [c] δ(P), $^1J(PtP)$, and $^3J(PtP)$.

Table 3. Proton n.m.r.[a] and i.r. data[b]

Complex	$\delta(CH_2)$	$^3J(PtCH_2)$	$^2J(HH)$	$\nu(C\equiv N)$[c]	Others
(*a*) Platinum					
(2a)	4.6	33.4		2 132	
(6a)	4.54	36		2 115	
(8a)	4.67 4.07	36 32	13.9	2 125	ν(CO) 1 978
(8c)	5.12[d]	50		2 100	ν(CO) 2 030 ν(Ir–Cl) 270
(*b*) Palladium					
(2b)	4.26			2 130	
(8b)	4.42 4.18		12.2	n.o.	
(8d)	4.91 4.56		14.8	2 115	ν(CO) 2 020 ν(Ir–Cl) 268
(9a)	4.04 3.42		13.7	2 130	ν(CO) 1 990, 1 890, 1 860

[a] δ values in p.p.m. to high frequency of $SiMe_4$, *J* values (±1 Hz) in Hz. Measured in CD_2Cl_2 at *ca.* 20 °C. [b] ±2 cm^{-1} as Nujol mulls. Other data are in the Discussion section. [c] All very weak or not observed (n.o.). [d] Not resolved into a multiplet even at −50 °C.

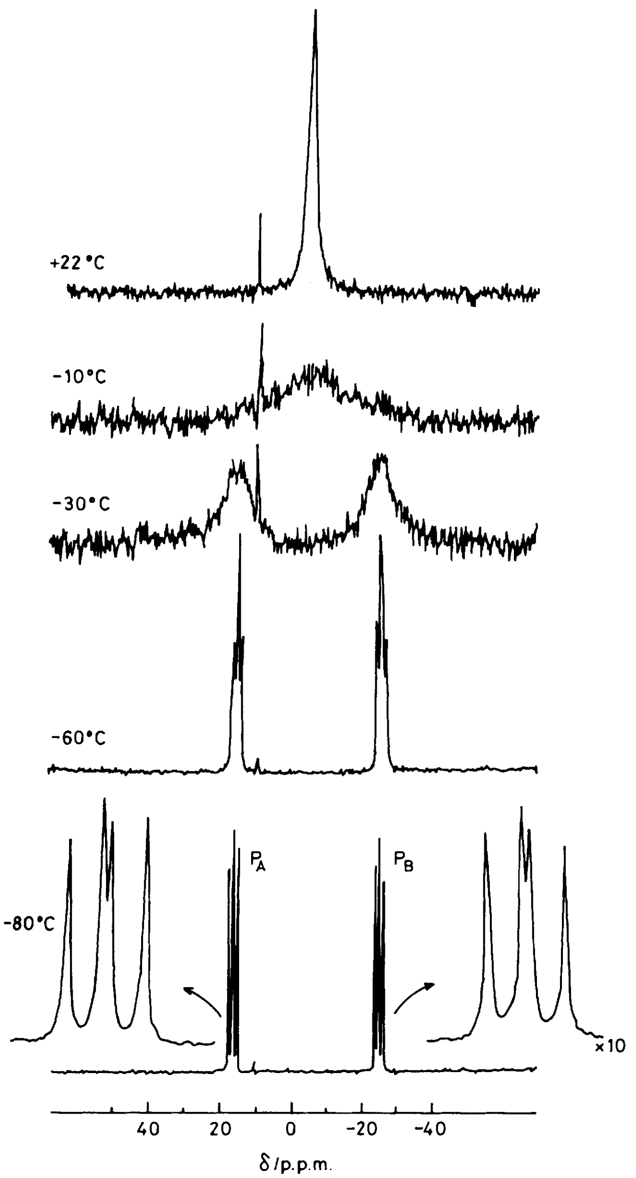


Figure. $^{31}P-\{^1H\}$ N.m.r. spectrum of the fluxional complex *trans*-$[Pd(CN)_2(dppm\text{-}P)_2]$. The sharp peak at δ = *ca.* 10 p.p.m. is due to an impurity

i.r. spectrum which shows a band at 1 978 cm^{-1}, assigned to ν(CO), and one at 2 125 cm^{-1}, assigned to ν(CN). The diacyanopalladium–rhodium analogue was made and characterized similarly as (**8b**). The analogous platinum–rhodium diacetylide complexes are ionic and of type $[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Rh(CO)]Cl$ with the acetylide group 'endways on' to Pt but 'sideways on' to Rh. Presumably the cyanide complex (**8a**) is not ionic because CN shows a much smaller tendency to bond sideways on than does C≡CR. Treatment of the neutral complex (**8a**) with $AgPF_6$ in acetone gave an orange solution shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to be a mixture of three phosphorus-containing species. These were not identified but one of them may have been the desired cationic platinum–rhodium complex and had $\delta(P_A) = +0.85$ p.p.m., $^1J(PtP_A) = 2\,282$ Hz, $\delta(P_B) = +4.8$ p.p.m., $^1J(PtP_B) = 78$ Hz, and $^2J(P_AP_B) + {}^4J(P_AP_{B'}) = 39$ Hz.

We have also made the analogous Pt–Ir and Pd–Ir complexes, (**8c**) and (**8d**) respectively. The Pt–Ir complex was made from the dppm-*P* platinum complex (**1a**) and $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}p)]$; details in the Experimental section and characterizing data in Tables. The palladium analogue (**8d**) was made by displacing PPh_3 from *trans*-$[IrCl(CO)(PPh_3)_2]$ using $[Pd(CN)_2(dppm\text{-}P)_2]$ in benzene. It could also be made by treating $[Pd(CN)_2(dppm\text{-}P)_2]$ with $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}p)]$ in dichloromethane at *ca.* −50 °C.

Treatment of $[Pd(CN)_2(dppm\text{-}P)_2]$ with $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cyclohepta-1,3,5-triene) in dichloromethane at 0 °C gave a brown palladium–molybdenum heterobimetallic in good (66%) yield; further details are in the Experimental section, characterizing analytical and spectroscopic data in the Tables. This complex is formulated as (**9a**); from the dark brown colour it seems probable that there is metal–metal interaction. The ^1H n.m.r. spectrum at 20 °C showed non-equivalent methylene hydrogens indicative of some bridging interactions. It is possible that there is C≡N–Mo interaction although we could observe only one band in the i.r. absorption spectrum due to ν(C≡N) at 2 130w cm^{-1}; an i.r. absorption band due to bridging CN might be buried under the intense i.r. bands due to ν(C≡O). Complexes of the type $[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2M(CO)_3]$ have one bridging acetylene and one terminal acetylene and are fluxional,[1] whereas the dicyanide complex (**9a**) is not fluxional at 20 °C, showing an AB quartet for the CH_2 hydrogens (Table 3). The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**9a**) shows two 'N' doublets and two central resonances. The signal at higher frequency, *viz.* δ = + 38.4 p.p.m., is assigned to the P nuclei bonded to molybdenum since the chemical shift is very similar to that (+ 38.7 p.p.m.) of Mo-bonded P nuclei in $[(PhC{\equiv}C)_2Pd(\mu\text{-}dppm)_2Mo(CO)_3]$ and the P nuclei bonded to palladium have a similar chemical shift (+ 19.6 p.p.m.) to those of the Pd-bonded P nuclei of the phenylacetylide complex (+ 16.4 p.p.m.). We have been unable to prepare the platinum–molybdenum analogue (**9b**) possibly because $[Pt(CN)_2(dppm\text{-}P)_2]$ is very much less soluble than its palladium analogue and has to be used in suspensions whereas the palladium complex can be used in solution, which gives better control over the course of a reaction.

Experimental

General methods were as previously described in recent papers from this laboratory.[12]

$[Pt(CN)_2(dppm\text{-}P)_2]$ (**1a**).—A solution of sodium cyanide (0.11 g, 2.24 mmol) in methanol (10 cm^3) was added dropwise to a solution of $[Pt(dppm\text{-}PP')_2]Cl_2{\cdot}EtOH$ (1.08 g, 1.00 mmol) in methanol (20 cm^3). A white precipitate formed rapidly and after 5 min it was filtered off, washed with water then with methanol, and dried *in vacuo*. Yield 0.95 g (94%). The complex $[Pd(CN)_2(dppm\text{-}P)_2]$ (**1b**) was made similarly. Yield 85%.

$[Pt_2(CN)_4(\mu\text{-}dppm)_2]$ (**2a**).—A mixture of $[PtCl_2(dppm\text{-}PP')]$ (1.04 g, 1.5 mmol) and sodium cyanide (0.15 g, 3.0 mmol) was suspended in ethanol (25 cm^3) and the mixture boiled for 14 h. The solvent was removed under reduced pressure and the residue triturated with methanol. The resultant solid was filtered off, washed with water and methanol, and dried *in vacuo*. Yield 0.88 g (91%).

$[Pd_2(CN)_4(\mu\text{-}dppm)_2]$ (**2b**).—A mixture of $[PdCl_2(dppm\text{-}PP')]$ (0.30 g, 0.53 mmol) and sodium cyanide (0.053 g, 1.07 mmol) in methanol (10 cm^3) was boiled for 3 h. The mixture was cooled and the resultant white precipitate collected, washed with methanol, water and methanol again, and dried. Yield 0.255 g, 89%. The complex was recrystallized from chloroform to give a chloroform solvate. Yield 0.25 g, 76%.

[Pt(dppm-*PP*′)$_2$][CN]$_2$ (**3a**).—The monohapto complex (**1a**) (0.1 g) was suspended in nitromethane (1.5 cm^3) or nitrobenzene (1.5 cm^3) and the mixture was heated to *ca.* 70 °C to give a yellow solution. The solution was then cooled and the product (**3a**) precipitated by the addition of diethyl ether. Yield 0.05 g, 50%.

[(NC)$_2$Pt(μ-dppm)$_2$AgI] (**5a**).—A solution of silver nitrate (0.020 g, 0.1 mmol) in water (*ca.* 0.1 cm^3) and acetone (10 cm^3) was added to a solution of complex (**1a**) (0.105 g, 0.1 mmol) in dichloromethane (5 cm^3). The resultant solution was evaporated to dryness under reduced pressure and the residue dissolved in acetone (*ca.* 8 cm^3) and treated with a solution of sodium iodide (0.10 g) in acetone (5 cm^3). The yellow solid which formed was filtered off, washed with aqueous sodium iodide solution, water, and methanol, and dried *in vacuo*. Yield 76%.

[(NC)$_2$Pt(μ-dppm)$_2$Au]Cl (**6a**).—A solution of [AuCl(PPh$_3$)] (0.097 g, 0.20 mmol) in dichloromethane (5 cm^3) was added to a suspension of complex (**1a**) (0.20 g, 0.20 mmol) in dichloromethane (5 cm^3). The mixture was warmed to give a clear solution and then diethyl ether was added. This gave the required product which formed white needles from dichloromethane–methanol. Yield 0.24 g, 97%.

[(NC)$_2$Pt(μ-dppm)$_2$HgCl$_2$] (**7a**).—A solution of [Pt(dppm-*PP*′)$_2$]Cl$_2$ (0.25 g, 0.24 mmol) in hot ethanol (10 cm^3) was treated with Hg(CN)$_2$ (0.061 g, 0.24 mmol) in ethanol (5 cm^3). The required complex separated after a few seconds and was isolated by filtration, washed with ethanol, and dried. Yield 0.30 g, 95%.

An identical product was formed by heating complex (**1a**) in benzene with a solution of mercury(II) chloride in tetrahydrofuran. The mixture was warmed for a few minutes and the product isolated by filtration, *etc.* Yield 79%.

[(NC)$_2$Pd(μ-dppm)$_2$Rh(CO)Cl] (**8b**).—A solution of [Rh$_2$Cl$_2$(CO)$_4$] (0.008 g, 0.021 mmol) in dichloromethane (1 cm^3) was added to a cooled (−10 °C) solution of *trans*-[Pd(CN)$_2$(dppm-*P*)$_2$] (0.039 g, 0.042 mmol) in dichloromethane (5 cm^3) to give an orange solution with evolution of CO. The solvent was removed under reduced pressure and the residue was triturated with diethyl ether to give the orange-brown product. Yield 0.035 g, 76%.

The platinum analogue (**8a**) was prepared similarly in 82% yield.

[(NC)$_2$Pt(μ-dppm)$_2$Ir(CO)Cl] (**8c**).—To a stirred suspension of [Pt(CN)$_2$(dppm-*P*)$_2$] (0.608 g, 0.60 mmol) in degassed benzene (30 cm^3) was added [IrCl(CO)$_2$(NH$_2$C$_6$H$_4$Me-*p*)] (0.236 g, 0.60 mmol), to give a yellow-brown suspension. This was heated under reflux for 18 h, cooled, filtered, and the filtrate evaporated to *ca.* 5 cm^3 under reduced pressure and cooled to *ca.* +4 °C. This gave the required product as yellow microcrystals. Yield 0.28 g, 37%.

[(NC)$_2$Pd(μ-dppm)$_2$Ir(CO)Cl] (**8d**).—A solution of *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0.025 g, 0.032 mmol) in degassed benzene (1 cm^3) was added to a suspension of [Pd(CN)$_2$(dppm-*P*)$_2$] (0.03 g, 0.032 mmol) in degassed benzene (1 cm^3). The resultant yellow suspension was heated under reflux to give an orange solution which was heated for a further 1 h. The mixture was cooled to give the required product as orange microcrystals. Yield 0.032 g, 84%.

[(NC)$_2$Pd(μ-dppm)$_2$Mo(CO)$_3$] (**9a**).—A solution of [Mo(CO)$_3$(C$_7$H$_8$)] (0.071 g, 0.26 mmol) in dichloromethane (2 cm^3) was added at 0 °C to a solution of [Pd(CN)$_2$(dppm-*P*)$_2$] (0.24 g, 0.26 mmol) in dichloromethane (2 cm^3). The solution became orange immediately but then changed to brown after 10 s. The mixture was stirred at 0 °C for a further 2 h and then methanol (30 cm^3) was added and the mixture reduced in volume to *ca.* 20 cm^3 under reduced pressure. The required product separated as brown microcrystals which were filtered off, washed with methanol, *etc.* Yield 0.189 g, 66%.

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